## 23. *Organosilicon Compounds. Part XVIII.\* The Interaction of (Aryldimethylsilyl)methyl Chlorides and Sodium Ethoxide in Ethanol.*
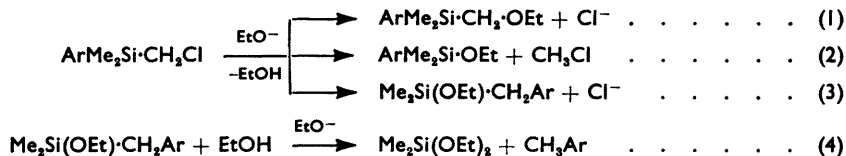
By C. Eaborn and J. C. Jeffrey.

When (aryldimethylsilyl)methyl chlorides, $X \cdot C_6H_4 \cdot SiMe_2 \cdot CH_2Cl$, react with sodium ethoxide in ethanol, toluene derivatives, $X \cdot C_6H_4 \cdot CH_3$, are formed along with products of substitution at the carbon atom and of cleavage of $Si\text{—}CH_2Cl$ bonds. These toluene derivatives are thought to arise from cleavage of the Si–benzyl bonds formed by intramolecular migration of the aryl group from silicon to the neighbouring carbon atom, the rearrangement being induced by nucleophilic attack of ethoxide ion on the silicon atom. The proportion of rearrangement for a series of $p$-substituted compounds falls in the order $(X =)$ $p$-Cl $> p$-Me $> p$-MeO $>$ H, but the rate of rearrangement is in the order $p$-Cl $>$ H $> p$-Me $> p$-MeO The rearrangement is thus facilitated by electron-withdrawal in the aryl group, as are also the substitution and cleavage reactions.

$p$-Chlorophenyl(ethoxymethyl)dimethylsilane with aqueous-ethanolic hydrofluoric acid gives 4-chlorobenzylfluorodimethylsilane, this being the first example of migration of an aryl group from silicon to carbon in a Wagner–Meerwein type of rearrangement.

CONTINUING our study [1] of the effect of an organosilyl group on the reactivity of an adjacent C—Hal bond we have examined the interaction of $RMe_2Si \cdot CH_2Cl$ compounds (R = Me or Ar) with sodium ethoxide in ethanol. We were primarily interested in substitution at carbon to give $RMe_2Si \cdot CH_2 \cdot OEt$, but we also expected cleavage of the $Si\text{–}CH_2Cl$ bonds, since Speier had shown that this occurs in the case of trimethylsilylmethyl chloride.[2] We were not prepared for the additional complication that when R is a phenyl or substituted phenyl group the toluene derivative $R \cdot CH_3$ forms a high proportion of the products, having been formed by a 1 : 2-migration of the aryl group from silicon to carbon followed by cleavage of the Si–benzyl bond thus formed.

*The Reaction Products.*—The reactions between (aryldimethylsilyl)methyl chlorides and ethanolic sodium ethoxide can best be described in terms of the following scheme : [3]

$$ArMe_2Si \cdot CH_2Cl \xrightarrow[-EtOH]{EtO^-} \begin{cases} ArMe_2Si \cdot CH_2 \cdot OEt + Cl^- & \quad\quad (1) \\ ArMe_2Si \cdot OEt + CH_3Cl & \quad\quad (2) \\ Me_2Si(OEt) \cdot CH_2Ar + Cl^- & \quad\quad (3) \end{cases}$$

$$Me_2Si(OEt) \cdot CH_2Ar + EtOH \xrightarrow{EtO^-} Me_2Si(OEt)_2 + CH_3Ar \quad\quad\quad (4)$$

Reactions (1), (2), and (4) are of known types, Speier having shown that trimethylsilylmethyl chloride and ethanolic ethoxide give diethoxydimethylsilane along with (ethoxymethyl)trimethylsilane,[2] and Eaborn and Parker having shown that the Si–benzyl bond is readily broken by alkali.[4] We have now shown that benzylethoxydimethylsilane is destroyed by ethanolic ethoxide, giving toluene, in much less time than is required for the reaction of (phenyldimethylsilyl)methyl chloride with this reagent, so it is unlikely that appreciable quantities of the benzyl(ethoxy)dimethylsilane product of reaction (3) will survive to be isolated.

The products were not isolated in the form required by the reaction scheme above, for after removal of the toluene derivative, $CH_3 \cdot Ar$, the residue was treated with aqueous-ethanolic hydrogen fluoride to convert into the corresponding fluorides, the ethoxysilanes

\* Part XVII, *J.*, 1956, 1436.

[1] Eaborn and Jeffrey, *J.*, 1954, 4266.
[2] Speier, *J. Amer. Chem. Soc.*, 1948, **70**, 4142.
[3] Eaborn and Jeffrey, *Chem. and Ind.*, 1955, 1041.
[4] Eaborn and Parker, *J.*, 1955, 126.

ArMe$_2$Si·OEt or Ar·CH$_2$·SiMe$_2$·OEt (both of which boil close to the ArMe$_2$Si·CH$_2$·OEt products), and any hydrolysis products of these formed in the isolation process. This led to complications as follows. (i) The silicon–aryl bonds in both (ethoxymethyl)- and ethoxy-$p$-methoxyphenyl-dimethylsilane were cleaved by the acid,[5] anisole and (ethoxymethyl)fluorodimethylsilane being obtained. (ii) Similar cleavage occurred of the $p$-tolyl group, but not of the phenyl or $p$-chlorophenyl group.[6] (iii) From ($p$-methyl- and $p$-chloro-phenyldimethylsilyl)methyl chloride some fluoro-4-methyl- and fluoro-4-chlorobenzyl-dimethylsilane, respectively, were obtained. While these fluorides might have come from benzylethoxydimethylsilane products of reaction (3), we have found that $p$-chloro- and $p$-methyl-phenyl(ethoxymethyl)dimethylsilane give the rearranged fluorides $p$-Cl·C$_6$H$_4$·CH$_2$·SiMe$_2$F and $p$-Me·C$_6$H$_4$·CH$_2$·SiMe$_2$F on treatment with hydrofluoric acid, and we believe it safer to assume that all of the benzyldimethylsilyl fluoride product arises in this way. Calculations will be mainly based on this assumption, but even if the whole of these fluorides actually come from products of reaction (3) no argument or conclusion below need be altered. It is also assumed that no appreciable cleavage of Si–CH$_2$·OEt bonds occurs; this is partly justified by the fact that Si–CH$_2$·OMe bonds are stable to methoxide ion in methanol (see Experimental section and ref. 2). The 4-chlorobenzyl–silicon bond would be particularly unlikely to survive the reaction with ethanolic ethoxide,[4] but the 4-methylbenzyl–silicon bond is more resistant to alkaline cleavage and it is possible that part of the rearranged fluoride, $p$-Me·C$_6$H$_4$·CH$_2$·SiMe$_2$F, comes from the silicon ethoxide produced in reaction (3).

Table 1 summarises the proportions of products of substitution [reaction (1)], rearrangement [reaction (3)], and cleavage [reaction (2)], isolated from R·SiMe$_2$·CH$_2$Cl compounds, and also gives the percentages adjusted to add to 100. (After consideration of probable mechanical losses we consider this simple adjustment to be the most satisfactory.)

TABLE 1.

| | Products isolated * (%) | | | | Reaction proportions | | |
|---|---|---|---|---|---|---|---|
| R | Substn. | Rearr. | Cleavage | Recovery | Substn. | Rearr. | Cleavage |
| C$_6$H$_5$ ................. | 42 | 32 | 16 | 90 | 47·3 | 34·7 | 18 |
| $p$-Cl·C$_6$H$_4$ ............. | 22 | 43 | 18 | 83 | 26·3 | 52·3 | 21·4 |
| $p$-CH$_3$·C$_6$H$_4$ ......... | 31·5 | 38·5 | 14 | 84 | 37·7 | 45·9 | 16·5 |
| $p$-CH$_3$O·C$_6$H$_4$ ......... | 30·5 | 35·5 | 16·5 | 83 | 36·9 | 43·2 | 19·9 |

\* From reaction at the b. p. of the mixture (*i.e.*, *ca.* 78°).

Sodium methoxide in boiling methanol causes no detectable cleavage of (phenyldimethylsilyl)methyl chloride but gives 76% of substitution product and 19% of rearrangement product (toluene).

*Kinetic Studies.*—The reactions of $n$-butyl chloride and organosilylmethyl chlorides R·CH$_2$Cl with sodium ethoxide in ethanol were followed by titration of the chloride ion produced. Good second-order kinetics were observed, and the results are summarised in Table 2, in which rate-constants (l. hr.$^{-1}$ mole$^{-1}$) and the apparent Arrhenius energies of activation, $E$, are listed. The variations in $E$ within the group of organosilicon compounds are not significant, but the trend of values follows the trend in rate constants.

TABLE 2.

| R′ | Pr$^n$ | SiMe$_3$ | SiPhMe$_2$ | SiMe$_2$·C$_6$H$_4$Cl-$p$ | SiMe$_2$·C$_6$H$_4$Me-$p$ | SiMe$_2$·C$_6$H$_4$·OMe-$p$ |
|---|---|---|---|---|---|---|
| 10$k_2$ (79·6°) ...... | 4·42 | 1·25 | 1·63 | 6·61 | 1·16 | 1·18 |
| 10$k_2$ (71·3°) ...... | 1·91 | 0·50 | 0·67 | 2·89 | 0·46 | 0·48 |
| $E$ (kcal. mole$^{-1}$) | 24·3 | 26·6 | 25·8 | 24·0 | 26·8 | 26·1 |

When held in the system (as in our kinetic experiments) any methyl chloride formed reacts with the ethoxide several times more rapidly than do the original halides, and thus

[5] Eaborn, *J.*, 1953, 3148.
[6] Cf. Eaborn, *J.*, 1956, 4858.

simple second-order kinetics result from three simultaneous bimolecular reactions (1), (2), and (3) of the (aryldimethylsilyl)methyl chlorides.

The rates of substitution, rearrangement, and cleavage may be worked out by using the overall rates at 79·6° (Table 2) and the product data of Table 1, the temperature of the reaction system used for product data (slightly greater than 78°, the b. p. of the solvent, because of the solutes present) being sufficiently close to that used for kinetics. The results are shown in Table 3, which refers to reaction of $R \cdot CH_2Cl$ compounds at 79·6°.
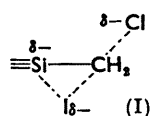
TABLE 3. *Second-order rate constants* (l. hr.$^{-1}$ mole$^{-1}$).

| R | Substitution | Rearrangement | Cleavage |
|---|---|---|---|
| $Pr^n$ ..................................................... | 0·442 [*] | — | — |
| $SiMe_3$ [b] ............................................. | 0·11 | — | 0·017 |
| $SiMe_2 \cdot C_6H_5$ ...................................... | 0·077 | 0·057 | 0·029 |
| $SiMe_2 \cdot C_6H_4Cl\text{-}p$ ................................ | 0·17 (0·14) [c] | 0·35 (0·38) [c] | 0·14 |
| $SiMe_2 \cdot C_6H_4Me\text{-}p$ ............................... | 0·044 (0·038) [c] | 0·053 (0·058) | 0·019 |
| $SiMe_2 \cdot C_6H_4 \cdot OMe\text{-}p$ .......................... | 0·043 | 0·051 | 0·023 |

[*] Elimination, which probably contributes <10% to the rate, has been neglected. [b] Speier's product data have been used, *viz.* 86·5% substitution and 13·5% cleavage.[2] [c] The figures in parentheses would apply if the whole of the benzyldimethylsilyl fluoride products came from the initial product of the rearrangement reaction.

It will be noticed that while the proportion of rearrangement falls in the order (R = ) $p\text{-}Cl \cdot C_6H_4 > p\text{-}Me \cdot C_6H_4 > p\text{-}MeO \cdot C_6H_4 > C_6H_5$, the rate of rearrangement falls in the order $p\text{-}Cl \cdot C_6H_5 > C_6H_5 > p\text{-}Me \cdot C_6H_4 > p\text{-}MeO \cdot C_6H_4$, *i.e.*, in the order of increasing electron-release in R.

*The Substitution Reaction.*—The C–Cl bond in trimethylsilylmethyl chloride is about 4 times less reactive towards ethoxide ion than that in *n*-butyl chloride and thus (by reasoning from relative reactivities of alkyl bromides [7]) *ca.* 16 times less reactive than that in ethyl chloride. Thus while replacement of the methyl group in ethyl chloride by the trimethylsilyl group increases reactivity towards $S_N2$ substitution by iodide ion in acetone it decreases reactivity towards $S_N2$ substitution by ethoxide ion in ethanol. We have previously postulated that a trimethylsilyl group activates in the halogen-exchange reaction because the attacking ion can partly co-ordinate with silicon in a transition state such as (I), and that this effect overcomes the deactivating effect which might be expected to result from the inductive release of electrons from silicon towards the C–Cl bond, which causes additional repulsion of the attacking agent.[1] In the ethoxide ion reaction a transition state similar to (I) might be less easily formed, since the small oxygen atom would have to bridge the relatively long Si–C bond, so that the inductive effect would be of great importance and lead to overall deactivation. In agreement, additional electron-withdrawal in the organosilyl group increases the rate of reaction.

The problem of the influence of neighbouring organosilyl groups on reactivity of C–Hal bonds has recently been complicated by the observation that in iodide-ion exchange in aqueous ethanol trimethylsilylmethyl iodide is several times *less* reactive than ethyl iodide.[8]

*The Cleavage Reaction.*—Replacement of a methyl of the trimethylsilyl group by a phenyl group increases the ease of cleavage of the Si–CH$_2$Cl bond. This is in line with the greater ease of alkaline cleavage of the silicon–benzyl bond in $p$-(phenyldimethylsilyl)-methylbenzoic acid than of that in the corresponding trimethylsilyl conpound,[9] and reflects the increased ease of nucleophilic attack on silicon. The introduction of the $p$-Cl group increases the rates of cleavage and rearrangement (both involving a nearer reaction

[7] Dhar, Hughes, Ingold, and Masterman, *J.*, 1948, 2055.
[8] Miller, Neiman, Savitskii, and Mironov, *Doklady Akad. Nauk S.S.S.R.*, 1955, **101**, 495 (*Chem. Abs.*, 1956, **50**, 3217).
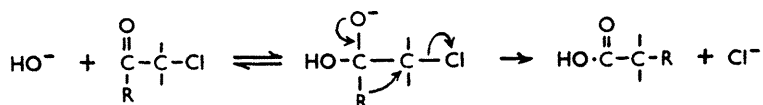[9] H. R. Allcock, Thesis, London, 1956.

centre) more than that of substitution, so that the proportion of the latter reaction falls markedly.

The lack of detectable cleavage of (phenyldimethylsilyl)methyl chloride by methanolic methoxide agrees with Speier's observations [2] on trimethylsilylmethyl chloride. It is probable that increase in the ease of the substitution reaction at carbon mainly causes predominance of this reaction rather than any marked decrease in the ease of cleavage or rearrangement.

*The Rearrangement Reaction.*—There are several examples of intramolecular migrations of alkyl groups from a silicon atom to an adjacent carbon atom induced by electron-deficiency at the latter, the rearrangements being of the Wagner–Meerwein type.[10] The migrations we now report are the first examples of organosilicon rearrangements brought about by a nucleophilic reagent, and the first involving aryl groups. That the migration in intramolecular is shown by the exclusive formation of *o*- and *m*-xylene, respectively, from (*o*- and *m*-tolyldimethylsilyl)methyl chloride, and of *p*-substituted toluenes from all the *para*-compounds described above.
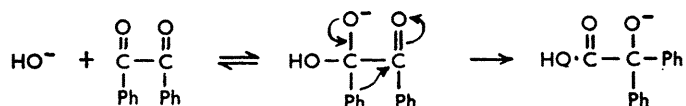
It is clear that rearrangement is induced by nucleophilic attack on silicon, leading to an electron-excess at the silicon atom. The overall change, *viz.*, replacement of a C–Cl bond by the much stronger Si–O bond is thermodynamically highly favoured.

The rearrangement could be either a synchronous process (*a*), or a two-step process (*b*). [In both cases the separation of chloride ion is written as being synchronous with the movement of the phenyl group; in (*b*) the chloride ion could separate in a slow step before the phenyl migrates, but this is less likely.]

$$(a) \quad EtO^- \quad SiMe_2{-}CH_2{-}Cl \quad \longrightarrow \quad EtO \cdot SiMe_2 \cdot CH_2Ar \ + \ Cl^-$$
$$\underset{Ar}{|}$$

$$(b) \quad EtO^- \ + \ SiArMe_2 \cdot CH_2Cl \quad \underset{}{\overset{Fast}{\rightleftharpoons}} \quad EtO \cdot \bar{S}iArMe_2 \cdot CH_2Cl$$

$$EtO \cdot \bar{S}iMe_2{-}CH_2{-}Cl \quad \overset{Slow}{\longrightarrow} \quad EtO \cdot SiMe_2 \cdot CH_2Ar \ + \ Cl^-$$
$$\underset{Ar}{|}$$

The synchronous mechanism (*a*) is of a general type postulated by Ingold but not known,[11] while the step-wise process (*b*) shows analogies to the " benzilic " mechanism proposed for some Favorskii rearrangements : [12]

$$HO^- \ + \ \underset{R}{\overset{O}{\underset{|}{\overset{||}{C}}}}{-}\overset{|}{\underset{|}{C}}{-}Cl \quad \rightleftharpoons \quad HO{-}\overset{O^-}{\underset{R}{\overset{|}{C}}}{-}\overset{|}{\underset{|}{C}}{-}Cl \quad \longrightarrow \quad HO \cdot \overset{O}{\underset{|}{\overset{||}{C}}}{-}\overset{|}{\underset{|}{C}}{-}R \ + \ Cl^-$$

and, less obviously, to the benzilic acid rearrangement : [13]

$$HO^- \ + \ \underset{Ph}{\overset{O}{\underset{|}{\overset{||}{C}}}}{-}\underset{Ph}{\overset{O}{\underset{|}{\overset{||}{C}}}} \quad \rightleftharpoons \quad HO{-}\underset{Ph}{\overset{O^-}{\underset{|}{\overset{|}{C}}}}{-}\underset{Ph}{\overset{O}{\underset{|}{\overset{||}{C}}}} \quad \longrightarrow \quad HO \cdot \overset{O}{\underset{|}{\overset{||}{C}}}{-}\underset{Ph}{\overset{O^-}{\underset{|}{\overset{|}{C}}}}{-}Ph$$

It is convenient and justifiable [14] to discuss the rearrangement in terms of the quinque-covalent-silicon intermediate of process (*b*), even though this may not have existence [its energy being so high that the potential energy profile of the reaction merges into that

[10] Whitmore, Sommer, and Gould, *J. Amer. Chem. Soc.*, 1947, **69**, 1976; Sommer, Bailey, Gould, and Whitmore, *ibid.*, 1954, **76**, 801; Sommer, and Evans *ibid.*, p. 1186.
[11] Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell and Son, London, 1953, p. 518.
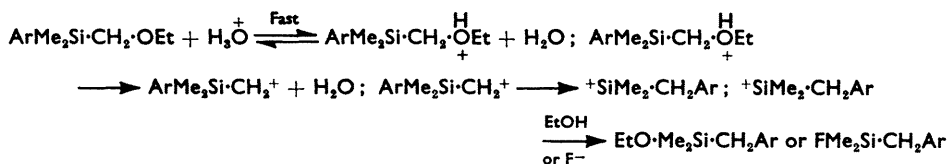[12] Tchoubar, *Bull. Soc. chim. France*, 1955, 1363.
[13] Alexander, " Principles of Ionic Organic Reactions," Wiley and Son Inc., New York, 1950, p. 199.
[14] Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.

of process (*a*)]. Since this intermediate is of high energy compared with that of the reactants and products, the transition state for its decomposition will be close to it in energy and structure, and substituent-influences will be much the same on both intermediate and transition state. The intermediate, in which the silicon atom bears a negative charge, will clearly be stabilised by electron-withdrawal from silicon, and the transition state will be stabilised in like manner. Thus migration of the phenyl group will be facilitated by electron-withdrawing substituents, as in the benzilic acid rearrangement,[14, 15] but contrary to what is found for the more common migrations of phenyl groups.

If the synchronous mechanism (*a*) is correct, then in the transition state the Si–O bond must be formed to a greater extent than the Si–Ar and C–Cl bonds are broken, so that the silicon is more negative in the transition state than in the ground state. This mechanism would be open in principle to organic compounds containing only saturated carbon atoms β- to the halogen (*i.e.*, Ph–$\overset{|}{C}$–$\overset{|}{C}$–Cl), and the availability for co-ordination of *d*-orbitals of silicon provides a simple explanation of the fact that while no such organic rearrangement is known the organosilicon rearrangement is a ready process.

*Rearrangements of (Ethoxymethyl)dimethylphenylsilanes.*—We have obtained a small yield of 4-chlorobenzylfluorodimethylsilane from treatment of *p*-chlorophenyl(ethoxymethyl)dimethylsilane with aqueous-ethanolic hydrogen fluoride. Similar rearrangement seems to occur with (ethoxymethyl)dimethyl-*p*-tolylsilane, although the rearranged fluoride was not isolated. The reactions can be written :

$$ArMe_2Si \cdot CH_2 \cdot OEt + H_3\overset{+}{O} \underset{}{\overset{Fast}{\rightleftharpoons}} ArMe_2Si \cdot CH_2 \cdot \overset{H}{\overset{+}{O}Et} + H_2O \; ; \; ArMe_2Si \cdot CH_2 \cdot \overset{H}{\overset{+}{O}Et}$$

$$\longrightarrow ArMe_2Si \cdot CH_3^+ + H_2O \; ; \; ArMe_2Si \cdot CH_2^+ \longrightarrow {}^+SiMe_2 \cdot CH_2Ar \; ; \; {}^+SiMe_2 \cdot CH_2Ar$$

$$\overset{EtOH}{\underset{or \; F^-}{\longrightarrow}} EtO \cdot Me_2Si \cdot CH_2Ar \; or \; FMe_2Si \cdot CH_2Ar$$

(Ethoxy- or hydroxy-silane products would be subsequently converted into fluorides.) The carbonium and siliconium ions may never be completely free, nucleophilic attack on silicon (by solvent molecules or fluoride ions) possibly assisting the migration of the aryl group to the forming carbonium ion.

Although phenyl groups would be expected to migrate from silicon to carbon much more readily than alkyl groups in such Wagner–Meerwein rearrangements, no examples have been reported previously. Use of stronger acids would no doubt lead to more rapid rearrangement but would also increase the aryl–Si bond cleavage.

### EXPERIMENTAL

(Aryldimethylsilyl)methyl halides were prepared from chloro(chloromethyl)dimethylsilane and the appropriate arylmagnesium bromide in ether.[1] (o-*Tolyldimethylsilyl*)*methyl chloride* had b. p. 110°/5 mm., $n_D^{20}$ 1·5185 (Found : C, 60·9; H, 7·8. $C_{10}H_{15}ClSi$ requires C, 60·5; H, 7·6%), and the m-*isomer* had b. p. 112°/5 mm., $n_D^{20}$ 1·5190 (Found : C, 60·6; H, 7·8%).

Because this method of preparation could produce Si–$CH_2Ar$ bonds, which with alkali would give the toluene derivative $ArCH_3$, the (aryldimethylsilyl)methyl chlorides were analysed by keeping samples in sealed tubes with excess of sodium ethoxide in ethanol for 7—10 days at 80° and then titrating the liberated chlorine ion. The chlorine content of all the halides was correct within 1%. Carbon and hydrogen analyses were also satisfactory, and the possible isomeric product, $Ar \cdot CH_2 \cdot SiMe_2Cl$, was shown to be absent in each case by the non-formation of chloride ion on treatment with aqueous alcohol.

*Kinetic Studies.*—Sodium was dissolved in anhydrous ethanol,[16] a weighed amount of the organic halide was added, and the solution was made up to 250 ml. The concentration of sodium ethoxide was determined by acid titration. Portions (5 ml.) were sealed in Pyrex test-tubes, which were then placed in a thermostat. After ½ hr. two tubes were withdrawn for

[15] Roberts, Smith, and Lee, *ibid.*, 1951, **73**, 618.
[16] Manske, *ibid.*, 1931, **53**, 1104.

the " zero-time " samples and further tubes (two each time) were withdrawn at intervals. They were quickly broken under water, the solution was made neutral with dilute nitric acid, and chloride ion was titrated potentiometrically by use of a Ag/AgCl electrode balanced (through an agar-agar salt bridge) against a quinhydrone electrode.

The typical run shown refers to trimethylsilylmethyl chloride (initially 0·0550M) and sodium ethoxide (initially 0·1378M) at 79·6°, 5 ml. portions being titrated against 0·01030M-silver nitrate. All reactant concentrations are corrected for expansion between room temperature and 79·6° (factor 1·074).

| Time, $t$ (hr.) ......... | 0 | 10 | 17 | 24.75 | 34.5 | 41.5 | 46.5 | 59 | 89 |
|---|---|---|---|---|---|---|---|---|---|
| Titre (ml.) ............ | 1·11 | 5·24 | 7·90 | 10·20 | 12·40 | 13·85 | 14·85 | 17·12 | 20·08 |
| $10^2$[RCl] (M) ......... | 5·29 | 4·495 | 3·99 | 3·55 | 3·12 | 2·84 | 2·65 | 2·22 | 1·65 |
| 10[NaOEt] (M) ...... | 1·357 | 1·28 | 1·23 | 1·18 | 1·14 | 1·11 | 1·09 | 1·05 | 0·99 |
| $10k_2$ (hr.$^{-1}$ mole$^{-1}$ l.) | — | 1·24 | 1·23 | 1·28 | 1·24 | 1·23 | 1·22 | 1·23 | 1·17 |

With trimethylsilylmethyl chloride, variation in initial concentrations of reactants caused little change in the rate constant at 79·6°: [RCl] = 0·055M, [NaOEt] = 0·14M, $k$ = 0·124; [RCl] = 0·1M, [NaOEt] = 0·13M, $k$ = 0·123; [RCl] = 0·10M, [NaOEt] = 0·37M, $k$ = 0·127 hr.$^{-1}$ mole$^{-1}$ l. Similar behaviour was found with the (phenyldimethylsilyl)methyl chloride ([RCl] = 0·045M, [NaOEt] = 0·32M, $k$ = 0·167; [RCl] = 0·031M, [NaOEt] = 0·16M, $k$ = 0·159 hr.$^{-1}$ mole$^{-1}$ l.) and with *n*-butyl chloride. Salt effects are clearly small and the initial concentrations were not varied for the remaining halides.

The following approximate initial concentrations were employed :

| R ...................................... | *p*-Cl·C$_6$H$_4$ | *p*-Me·C$_6$H$_4$ | *p*-MeO·C$_6$H$_4$ |
|---|---|---|---|
| [RMe$_2$Si·CH$_2$Cl] (M) ............................ | 0·05 | 0·04 | 0·28 |
| [NaOEt] (M) ...................................... | 0·29 | 0·31 | 0·60 |

*Product Analyses.*—The procedure will be described in detail for only one halide. A centred-rod column (efficiency, *ca.* 15 theoretical plates) of small hold-up was used for fractionations. Reaction times were sufficient for at least 99·5% reaction. Acid equivalents of organosilyl fluorides were determined by adding weighed samples to excess of aqueous-ethanolic alkali and back-titrating the excess of alkali.

(*a*) A solution of sodium (20 g.) and (phenyldimethylsilyl)methyl chloride (25 g., 0·135 mole) in ethanol was boiled for 30 hr., moisture being kept out by a guard tube (P$_2$O$_5$) fitted to the reflux condenser. Light petroleum (b. p. < 40°) was then added to the cooled mixture, and salts and ethanol were extracted with water. The aqueous extracts were extracted several times with further light petroleum before and after acidification (the latter being to destroy any sodium silyloxides present) and the combined petroleum extracts were washed, dried (Na$_2$SO$_4$) and fractionated, to give toluene (3·9 g., 0·042 mole, 32%), b. p. 110—111°, $n_D^{25}$ 1·4945 (which was identified by its ultraviolet absorption spectrum and by nitration to 2 : 4-dinitrotoluene). The residue was dissolved in ethanol (100 ml.), aqueous 40% w/w hydrofluoric acid (30 ml.) was added, and the mixture was kept just below its b. p. for 12 hr., a further quantity of ethanol (50 ml.) and acid (15 ml.) being added after 6 hr. The mixture was poured into excess of water, and ether-extraction followed by washing, drying (Na$_2$SO$_4$), and fractionation of the extract gave fluorodimethylphenylsilane (3·3 g., 0·0214 mole, 16%), b. p. 161—162°, $n_D^{25}$ 1·4712,* and (ethoxymethyl)dimethylphenylsilane (11 g., 0·057 mole, 42%), b. p. 220—222°, $n_D^{25}$ 1·4945 (Found : C, 68·2; H, 9·2. C$_{11}$H$_{18}$OSi requires C, 67·9; H, 9·4%).

(*b*) A solution of (*p*-chlorophenyldimethylsilyl)methyl chloride (36 g.) and sodium (30 g.) in ethanol (700 ml.) was boiled for 6 hr. *p*-Chlorotoluene (9 g.), b. p. 161—162°, m. p. and mixed m. p. 7·0—7·5° (giving *p*-chlorobenzoic acid on oxidation), was obtained. After treatment of the residue with hydrofluoric acid (40 ml. of acid and 150 ml. of ethanol for 12 hr.) there were obtained p-*chlorophenylfluorodimethylsilane* (5·5 g.), b. p. 198°, $n_D^{25}$ 1·4930 (Acid equiv., 189. Cl·C$_6$H$_4$·SiMe$_2$F requires equiv., 188·7), 4-*chlorobenzylfluorodimethylsilane* (1·5 g.), b. p. 217° $n_D^{25}$ 1·4955 (Acid equiv., 203. Cl·C$_6$H$_4$·CH$_2$·SiMe$_2$F requires equiv., 202·7), and p-*chlorophenyl-* (*ethoxymethyl*)*dimethylsilane* (6·5 g.), b. p. 258—260°, $n_D^{25}$ 1·5052 (Found : C, 58·1; H, 7·3. C$_{11}$H$_{17}$OClSi requires C, 57·7; H, 7·5%).

If the 4-chlorobenzylfluorodimethylsilane comes from interaction of *p*-chlorophenyl(ethoxymethyl)dimethylsilane and the hydrofluoric acid, then the above figures correspond to 21·8%

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* In a previous report [17] of this compound the value of $n_D^{25}$ should read 1·4710 and not 1·4110.
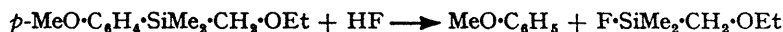
[17] Eaborn *J.*, 1953, 494.

of substitution, 43·3% of rearrangement, and 17·7% of cleavage. If this fluoride comes from 4-chlorobenzyldimethylsilyl ethoxide then the figures represent 17·3% of substitution, 47·8% of rearrangement, and 17·7% of cleavage.

(*c*) A solution of (*p*-methoxyphenyldimethylsilyl)methyl chloride (17·8 g.) and sodium (18 g.) in ethanol (400 ml.) was boiled for 60 hr.

A small amount (*ca.* 0·5 g.) of liquid of b. p. 153—155° was obtained (probably anisole) and methyl *p*-tolyl ether (3·6 g.), b. p. 174—175° (giving anisic acid, m. p. and mixed m. p. 184°, on oxidation). After the hydrofluoric acid treatment (30 ml. of acid and 100 ml. of ethanol for 12 hr., with 15 ml. of acid and 50 ml. of ethanol added after 6 hr.), fractionation gave (*ethoxymethyl*)*fluorodimethylsilane* (3·3 g.), b. p. 88—89°, $n_D^{20}$ 1·3710 (Acid equiv., 136. EtO·CH$_2$·SiMe$_2$F requires equiv., 136·2), and anisole (4·3 g.), b. p. 154°. A further 0·3 g. of liquid boiled between 160° and 200° leaving a residue of 0·4 g.

The (ethoxymethyl)fluorodimethylsilane must have been produced along with an equivalent amount of anisole (2·6 g.) by the (overall) reaction

$$p\text{-MeO·C}_6\text{H}_4\text{·SiMe}_2\text{·CH}_2\text{·OEt} + \text{HF} \longrightarrow \text{MeO·C}_6\text{H}_5 + \text{F·SiMe}_2\text{·CH}_2\text{·OEt}$$

The remaining anisole (1·7 g.) obtained after the hydrofluoric acid treatment must have come from ethoxy-*p*-methoxyphenyldimethylsilane Thus the products correspond to 35·5% of rearrangement, 30·3% of substitution, and 16·3% of cleavage.

(*d*) A solution of (*p*-tolyldimethylsilyl)methyl chloride (31·8 g.) and sodium (25 g.) in ethanol (600 ml.) was boiled for 36 hr. *p*-Xylene (6·5 g.), b. p. 138°, m. p. and mixed m. p. 13—14° (giving 2 : 3 : 5-trinitro-*p*-xylene, m. p. 137°, on nitration) was obtained. After the hydrofluoric acid treatment (150 ml. of ethanol and 40 ml. of acid for 12 hr., with 50 ml. of ethanol and 10 ml. of acid added after 6 hr.), fractionation gave 4·0 g. of material of b. p. 85—90°, toluene (1·8 g.), b. p. 110°, $n_D^{25}$ 1·4944, *fluorodimethyl-4-methylbenzylsilane* (1·1 g.), b. p. 201°, $n_D^{25}$ 1·4775 (Acid equiv., 182. CH$_3$·C$_6$H$_4$·CH$_2$·SiMe$_2$F requires equiv., 182), and (*ethoxymethyl*)-*dimethyl-p-tolylsilane* (4·5 g.), b. p. 243—244°, $n_D^{25}$ 1·4995 (Found : C, 69·6; H, 9·4. C$_{12}$H$_{20}$OSi requires C, 69·2; H, 9·7%).

The liquid of b. p. 85—90° was shown to contain toluene (an azeotrope of which with water boils at 85°) by oxidation of a sample to benzoic acid; the remainder was (ethoxymethyl)-fluorodimethylsilane, titration against alkali showing 3·1 g. of this to be present and thus 0·9 g. of toluene. The total amount of toluene formed in the hydrofluoric acid treatment is thus 2·7 g., and of this 2·1 g. [equiv. to 3·1 g. of (ethoxymethyl)fluorodimethylsilane] must have come from cleavage of 4·7 g. of (ethoxymethyl)dimethyl-*p*-tolylsilane and 0·6 g. from cleavage of 1·1 g. of fluorodimethyl-*p*-tolylsilane.

These figures correspond to 31·3% of substitution, 38·3% of rearrangement, and 13·9% of cleavage if all the fluorodimethyl-*p*-tolylsilane comes from (ethoxymethyl)dimethyl-*p*-tolylsilane, and to 27·6% of substitution, 42·0% of rearrangement and 13·9% of cleavage if it comes from ethoxydimethyl-4-methylbenzylsilane.

*Rearrangement of* (*Dimethyltolylsilyl*)*methyl Chlorides.*—A solution of (dimethyl-*m*-tolyl silyl)methyl chloride (15·7 g.) and sodium (18 g.) in ethanol (400 ml.) was boiled under reflux. Light petroleum (b. p. < 40°) was added to the cooled solution and the mixture was extracted with water. The petroleum solution was dried and fractionated to give *m*-xylene (2·1 g.), b. p. 138—139°, identified by nitration to 2 : 4 : 6-trinitro-*m*-xylene, m. p. 182°, and by oxidation to *iso*phthalic acid, m. p. 344—346°. The residue was not examined.

(*b*) Similar treatment of the *o*-isomer (10·1 g.) with sodium (14 g.) and ethanol (300 ml.) gave *o*-xylene (1·3 g.), b. p. 143—144°, m. p. and mixed m. p. −25° (giving 4 : 5-dinitro-*o*-xylene, m. p. 71°, on nitration).

(*Dimethylphenylsilyl*)*methyl Chloride and Methanolic Methoxide.*—A solution of the halide (23·5 g.) and sodium (15 g.) in anhydrous methanol was boiled for 10 days. Light petroleum extracts were dried and fractionated, to give toluene (2·2 g., 19%), b. p. 110—111°, $n_D^{25}$ 1·4945, and (*methoxymethyl*)*dimethylphenylsilane* (17·5 g., 76%), b. p. 207—209°, $n_D^{20}$ 1·4954 (Found : C, 66·2; H, 9·1. C$_{10}$H$_{16}$OSi requires C, 66·6; H, 8·95%).

p-*Chlorophenyl*(*ethoxymethyl*)*dimethylsilane and Hydrofluoric Acid.*—A solution of the ether (4·4 g.) and hydrofluoric acid (40 ml. of 40 wt.-% acid) in ethanol (150 ml.) was kept just below its b. p. for 24 hr. The mixture was poured into water, and ether-extraction followed by fractionation gave *p*-chlorobenzylfluorodimethylsilane (0·5 g.), b. p. 216° (Acid equiv., 203).

When (ethoxymethyl)dimethyl-*p*-tolylsilane (3·5 g.) was similarly treated for 12 hr., there

was obtained 1 g. of liquid of b. p. 205—240° (*i.e.*, boiling below the starting material). A sample gave fluoride ion on hydrolysis and titration indicated the presence of 0·2 g. of fluorodimethyl-4-methylbenzylsilane (which has b. p. 201°).

*Benzylethoxydimethylsilane and Ethanolic Ethoxide.*—A solution of the organosilane (12·7 g.) and sodium (30 g.) in ethanol (800 ml.) was boiled for 3 hr. The mixture was poured into water, and ether-extraction followed by washing, drying, and fractionation of the extract gave toluene (5·5 g., 85%), b. p. 110—111°, and no residue.

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